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REVIEW ARTICLE

Biosorption of zinc ion: a deep comprehension

Vishal Mishra

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Abstract Massive industrialization and urbanization of civilization during the last few decades have made a thrust in heavy metal pollution in various water bodies. In past, various kinds of conventional metal ion remediation technologies, such as cementation, osmosis, reverse osmosis, ultrafiltration, etc., have been practised. However, most of these technologies are quite expensive, and lead to the generation of secondary chemical sludge. However, biosorption of heavy metal ions is significantly inexpensive and an eco-friendly technology. Among the series of heavy metals, zinc has gained the significant interest due to its toxicity and easy availability in water bodies. Biosorption of zinc in liquid phase by living, nonliving, conventional and non-conventional biosorbents has been practised extensively in the past. This literature review focuses on the recent trends practised in the field of biosorption of zinc from liquid phase. The present work provides deep insight into various aspects of biosorption of zinc by different mechanisms of biosorption, bioaccumulation, isotherm, kinetic and mechanistic modeling. An exhaustive comparison among different sorts of biomasses has also been given in the present work to enlist all the milestones of biosorption.

V. Mishra
Department of Chemical Engineering, University of Petroleum and Energy Studies, Dehradun 248007, India

V. Mishra (✉)
Department of Chemical Engineering, University of Petroleum and Energy Studies, Dehradun 24800, India
e-mail: vishal.biochemical@gmail.com

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Introduction

The rapid world industrialization had a significant impact on the natural water reservoir pollution due to enormous discharge of heavy metals in various water bodies (Rezic 2013; Mahdavi et al. 2013). One of the significant elements that contribute significantly to the water pollution is zinc. Zinc is one of the essential elements of enzymes, such as superoxide dismutase (Mukhopadhyay et al. 1998). The Comprehensive environment response, Compensation and Liability act—2007 (CERCLA) has ranked zinc at 74th position with respect to water pollution with total score of 932.89 points (Mishra et al. 2010). The European Union Dangerous Substance Directive (76/464/EEC) has categorized zinc as list 2 element (Arshad et al. 2008).

Very often, iron and copper accompany the zinc in the effluent discharged from various industrial units. The most prominent form of zinc available in industrial effluent is zinc ions (Mishra and Patel 2009). According to the list of organic and inorganic pollutants prepared by United States Environmental Protection Agency (USEPA), zinc has been kept in the list of toxic metals with other 13 metals (Kumar et al. 2006; Cesur and Balkaya 2007). The guidelines for the discharge of zinc in ground water, fresh water and estuaries mentioned by government agencies of various countries have been shown in Table 1. Heavy metals have been divided into three categories, namely toxic metals, precious metals and radionuclides. Zinc comes under the classification of toxic heavy metals (Wang and Chen 2009).

Table 1 Guidelines of framework delineated by various government agencies

Name of agency	Type of water	Limit of discharge (mg l^{-1})	References
World Health Organization (WHO)	Drinking water	5	Kumar et al. (2006); Mishra and Patel (2009); Mohan and Singh (2002)
Minimum National Standards (MINAS), Ministry of Environment and Forest, Government of India	Surface water	5	Srivastava et al. (2007)
Minimum National Standards (MINAS), Ministry of Environment and Forest, Government of India	Potable water	3	Srivastava et al. (2006)
Central Pollution Control Board, India	Wastewater	5	Naiya et al. (2009)
United States Environment Protection Agency	Drinking water	5	Naiya et al. (2009)

Zinc toxicity, remediation technologies and characterization of wastewaters

Zinc contamination, its sources and toxicity

Pollution due to various heavy metals is a matter of serious concern in the present scenario. The usage and importance of a heavy metal give a clear indication of pollution level in atmosphere. Zinc is essentially an important element for many growing economic sectors of the world, such as metallurgical operational units, electroplating industry, mining industry and mine drainage operations. Some specific sources of zinc pollution in natural water and reservoirs include effluents discharged from galvanization industry, wood preservative industry, rubber vulcanization plant, zinc and brass metal alloy industry, ceramics, textiles, brass plating, fertilizers, paint and pigments, and batteries industries (Abdelwaha et al. 2013; Lee et al. 2004; Arshad et al. 2008; Baig et al. 2009). Some more pronounced sites of zinc pollution include electroplating units and sites of acid mine drainages. Recently, over 620 mg l^{-1} of zinc has been reported in the effluent released from the abandoned copper mines in Monsanto, US (Volseky 2003).

The extensive mining activities in Nent Valley (UK) over two centuries for zinc had left the river water and land polluted tremendously. Usually in mine drainage, zinc is present in liquid phase as zinc ions. However, the mine drainage from Nent Valley has very high alkalinity, therefore, zinc persists in liquid phase as carbonate complex ($ZincCO_3$). The level of zinc that comes in Nent valley mine drainage ranges between 3 and 8 mg l^{-1} (Nuttall and Younger 2000). The sample obtained from mines in Oruro, Bolvia indicated the presence of 8,709.2 mg of zinc equivalent to 1.34 mM/500 ml (Alvarez et al. 2007).

Table 2 Concentration of zinc present in industrial wastewater

Waste	Metal	Concentration	References
Zinc ash	Zn	60–85 (wt %)	Jha et al. (2001)
Flux	Zn	5.6 (wt %)	Jha et al. (2001)
	$ZnCl_2$	48.1 (wt %)	
	ZnO	27.4 (wt %)	
Blowing waste	Zn	81 (wt %)	Jha et al. (2001)
	ZnO	16 (wt %)	
Contaminated aquatic environments	Zn	3.25–99.25 mg l^{-1}	Yang et al. (2013)

Concentration of zinc in storm water runoff with various others heavy metals ranged as zinc 0.008–0.720 mg l^{-1}, copper 0.001–0.079 mg l^{-1}, manganese 0.001–0.516 mg l^{-1} and lead 0.003–0.010 mg l^{-1}, respectively (Asaf et al. 2004;Vijayaraghavan et al. 2008). Walker et al. 1999 characterized the urban runoff as zinc (0.0007–22.0 mg l^{-1}), copper (0.00006–1.41 mg l^{-1}) and lead (0.00057–26.0 mg l^{-1}). Zinc contamination in natural environment has been found in 985 sites out of 1,662 national sites of priority risk identified by USEPA (Agency for Toxic Substances and Disease Registry 2005). Wastes containing zinc have been categorized as hazardous waste under the Basal convention and European Union (Agarwal et al. 2004). The secondary waste generated during the metallurgical operations, i.e., zinc ash, zinc dross, flux, flue dust from electric arc furnace, automobile junks and sludge, contains very high amount of zinc in the form of some sort of compound or derivatives.

Frequently, zinc in secondary waste is accompanied by various other toxic heavy metals. Table 2 shows the various concentrations of zinc in secondary waste of metallurgical industries. The rising requirement of alkaline zinc manganese batteries and their disposal has posed a more potent source of zinc pollution in the environment (Ostroski et al. 2009). Since zinc is involved in almost all-metal polishing and metallurgical works, zinc ions are most habitually encountered in wastewater treatment (Pejic et al. 2008). However, zinc is an essential element required for

the growth of plants, animals and humans (Sengil and Ozacar 2009). But, excessive intake of zinc can be fatal. Metal zinc is non-biodegradable and it accumulates in the body of the organism through food chain (Ucun et al. 2009). Toxicity of zinc has several reversible and irreversible effects on natural flora and fauna. For example, very low exposure of zinc is responsible for gastrointestinal disturbance, i.e., irritability, nausea, loss of appetite, metal fume fever and muscular stiffness (Lesmana et al. 2009; Bhattacharya et al. 2006; Vilar et al. 2007; Marin et al. 2009). The level of zinc beyond a threshold concentration in soil affects the fertility of soil very adversely (Agorboude and Navia 2009).

The exposure to zinc also leads to lethargy, hyperamylasemia, pancreatitis, cholestatic jaundice, anemia, thrombocytopenia, pulmonary edema, renal failure, circulation and neurological disturbances (Klein 2000; Marin et al. 2009). The concentration of 120-μM of zinc leads to the micronucleus induction in plant *Vicia faba* (Mishra et al. 2010). In case of aquatics, the ionic form of zinc is lethal to invertebrates and vertebrate fish (Shek et al. 2009). Small amount of free zinc ions can cause heavy damage to ambient environment, kill some microorganism and excessive intake of zinc can also cause the deficiency of other dietary minerals (Shek et al. 2009; Han et al. 2013).

The inhalation of zinc as particulate matter at work place and in an ambient environment leads to intoxication resulting in pale mucous membrane, jaundice, numerous Heinz bodies, anemia and pediatric asthma (Cooper 2008; Hirshon et al. 2008). The concentration of zinc determines its role as apoptosis blocker or apoptosis inducer. There are several examples where zinc has behaved as apoptosis or programmed cell death inducer (Formigari et al. 2007; Wilson et al. 2007). The genotoxic character of zinc has been demonstrated in microorganisms, i.e., *Salmonella typhimurium* and *Escherichia coli* (Codina et al. 2000). The pulmonary exposure to particulate-sized zinc particle and sub-chronic inhalation of zinc sulfate could be responsible for cardiotoxicity (Wallenborn et al. 2008, 2009). Various industrial sectors and anthropogenic sources contributed to the pollution of zinc in environment.

In Algeria, the effluent of zinc electroplating units contaminates the Mediterranean coast (Addour et al. 1999). In India, there are more than 5,000 foundry units producing waste foundry sand (WFS) containing very high amount zinc metal ions (Kaur et al. 2013). Some of the industries that cause zinc pollution in India are Binani Zinc in Kerala (Thomas 1998), Hindustan Zinc Limited in Rajasthan (Sharma 1989, 1998), Debari Smelter Plant Rajasthan (Solanki and Singh 1981; Sharma 1989; Basu and Swarnkar 1990; Bhatnagar and Jancy 1998; Jaju 1998), Zinc Lead smelter plant (Solanki and Singh 1981; Sharma 1998; Thomas 1998), Sun rise zinc Goa (Bhatnagar and Jancy 1998) and Bharat zinc. Most of these industries either dump their effluents in landfill sites or store in industrial premises in pond-like structures. Except zinc lead smelter plant, none of the industries had been found to be involved in recycling of zinc, and undoubtedly their effluents and leach residue containing huge amount of zinc ranging from 1.26 to 60 % of the total waste generated. Table 3 represents the concentrations of zinc present in wastewater discharging from various industrial sources. In UK, the average rate of acid waste production is about 32,000 tonnes per year from 87 sites. Acid waste of the pickling acid released from galvanization plants in UK contains 192,000 mg l^{-1} of zinc.

The acid waste is transported to special treatment facility, where all the valuable metals are being lost (Stocks et al. 2005). Usually, the industries involved in galvanization, other similar type of industries and acid mine drainage operations, recycle their effluents to recover the valuable metals. The recycling of effluents was done by electro dialysis, emulsion pertraction technology (EPT) (Carrea et al. 2008), membrane-based technologies, resin-

Table 3 Study of Zn released from various metallurgical units

Name of plant	Location	Effluent	Concentration (mg l^{-1})	References
Belos hot dip galvanization plant	Bielsko-Baila, Poland	Spent pickling acid	80,000	Grzeszczyk and Rosocka (2007)
ND	Minas Gerais state, Brazil	Spent pickling acid	70,200	Mansur et al. (2008)
			33,900	
ND	ND	Spent pickling acid	26,120	Csicsovszki et al. (2005)
ND	ND	Copper industry industrial effluent	142	Basha et al. (2009)
ND	ND	Acid mine drainage	1,800	Valiente et al. (1991)
			520	
		Spent pickling acid	81,986,520	Carrea et al. (2008)

ND not defined

Table 4 Limitations of various conventional metal ion remediation methodologies

Methodology	Shortcomings	References
Ion exchange	Input cost is very high and maintenance cost is very high	Aderhold et al. (1996)
Adsorption	Efficiency of the process depends on type of adsorbent and chemical pretreatments are required to improve performance of adsorbent	Crini (2005)
Chemical Precipitation	Input of chemicals is required, problem of secondary sludge generation, disposal of secondary chemical sludge	Aderhold et al. (1996); O'Connell et al. (2008)
Membrane separation and ultrafiltration	Input cost is very high, maintenance is very costly, fouling of membrane, operation cost is very high, limitation of flow rates and removal of other metal decrease in presence of other metals	Qin et al. (2002); Madaeni and Mansourpanah (2003)
Electrochemical treatments	Input cost is very high, filtration is required for removal of flocs, initial pH and current density of the solution are required to be adjusted	Kongsricharoern and Polprasert (1995), (1996)
Floatation	Input cost, maintenance cost and operation cost are very high	Rubio et al. (2002)
Chemical coagulation and flocculation	Input cost is very high, involves huge amount of chemicals and generation of secondary chemical sludge	Aderhold et al. (1996), O'Connell et al. (2008)

mediated ion exchange, electro chemical ion exchange (EIX), solvent extraction (Diaz and martin 1994; Kerney 1994a, b, 1997) and chemical precipitation, etc. Additionally, these technologies treat metal ions waste. It became evident from Tables 3 and 4 that the effluents from various industries contain huge amount of zinc and other heavy metals. The technologies used to recycle effluent require huge cost and their application leads to tremendous loss of metals. As mentioned earlier, the biosorption of heavy metals is quite advantageous over conventional treatment technologies. Therefore, the next few sections will deal with the types of biosorption, their mechanism, kinetics and pathways of metal binding.

Available technologies for the removal of zinc from wastewater and their limitations

There is a long chain of technologies involved in the removal of zinc or any other heavy metal from various types of industrial wastewater and mine drainage. These include chemical precipitation, solvent extraction, sulfide precipitation, membrane filtration, ion exchange, reverse osmosis, electro dialysis, oxidation–reduction, ultrafiltration, evaporation, chemical coagulation/floatation and flocculation, cementation, sorption, biosorption, phyto separation/remediation, activated sludge process, anaerobic–anoxic–oxic (A2O), heavy metal removal from biosurfactants, immobilized microorganisms in rotating biological contractor, solid–liquid–solid extraction, active filtration and high gradient magnetic separation (Cazon et al. 2012, Jhonson et al. 1982; Anand et al. 1985; Costely and Wallis 2003; Mulligan et al. 2001; Tuppurainen et al. 2002; Hammaini et al. 2003; Gavrilescu 2004; Berg et al. 2005; Chang et al. 2006; Wu et al. 2007; Grzeszczyk and Rosocka 2007; Tofan et al. 2008; Baig et al. 2009; Ucun et al. 2009; Sprynskyy 2009). The conventional zinc ion remedial technologies have some major technical shortcomings (Rodrigues et al. 2012, Vimala et al. 2011, Eccles 1999; Miretzky et al. 2006). Some of the shortcomings of the conventional methodologies of zinc ion remediation have been represented in Table 4. Against the conventional methodologies, the biosorption of heavy metals is an inexpensive, eco-friendly and efficient methodology. Biosorption process makes use of biomass or microorganism, hence the use of this methodology does not involve the generation of secondary chemical sludge. The biosorbents are readily available and they are quite efficient to remediate heavy metals below a threshold concentration 100 mg l^{-1}. In biosorption, the use of microorganism does not involve the supply of nutrients. Thus, the process of biosorption is extensively simple and does not require skilled labor.

Removal of zinc from aqueous solution by various methods

The nature of bonding between the adsorbate and the surface of the adsorbent distinguishes between the types of adsorption. Based on nature of bond or sharing of electrons, the biosorption of the metal ions on the surface of adsorbent is categorized as physical adsorption and chemical adsorption.

Physical adsorption

In physical adsorption or physiosorption, the particles of the adsorbent bind to the surface of the adsorbate via weak interaction (Vander walls forces) (Crowell 1966) and there is no rearrangement or sharing of electrons between adsorbate and adsorbent surface. The physisorption energy ranges between 2 and 10 kcal mol^{-1}. Additionally, Kuyucak and Volesky (1988) reported the biosorption of zinc on dead mass of algae, fungi and yeast, mediated by electrostatic interaction between ions and cell wall moieties of dead biomass.

Chemical adsorption

In chemical adsorption, the particles of the adsorbate bind to the adsorbent with strong bonds (covalent bond, ionic bond, etc.). The adsorbate particle perturbs its electronic configuration upon adsorption (Masel 1952). Typical chemisorption energy ranges between 15 and 100 kcal mol^{-1}. The chemisorption or chemical adsorption was mediated by various mechanisms such as ion exchange between cell wall moieties and adsorbate species, complexion of adsorbate particles with cell wall functional entities, precipitation, chelation, etc. Precipitation can work in dual mode, i.e., metabolism dependent or metabolism independent.

Biosorption and bioaccumulation

The removal of zinc and various other heavy metal ions such as cadmium, copper, lead, mercury, cobalt, nickel, etc. passively by dead biomass is called biosorption (Volesky and Holan 1995; Davis et al. 2003). This mechanism is mediated by the interaction of the cell wall functional groups and metal ions. The cell walls of microbial cells are made up of polysaccharides, lipids and proteins. These constituents play a diverse role in metal ion binding, i.e., these components create the sites for binding of metal ion. Biosorption process of metal ions is quite fast and independent of cell metabolism (Veglio and Belochini 1997; Kadukova and Vircikova 2005). This process is also known as passive biosorption. Intracellular accumulation of metal ions is called bioaccumulation. Bioaccumulation is usually mediated by binding of metal ions by intracellular compounds, methylation, intracellular precipitation and other mechanisms. Bioaccumulation is second part of metal ion sequestration in living cells. Since bioaccumulation belongs to active biosorption, the bioaccumulation may get influenced by metabolic inhibitors, change of temperature and lack of energy. Significant difference of metal ion binding energies has been found between biosorption and bioaccumulation. Biosorption involves ~ 21 kJ mol^{-1} activation energy whereas bioaccumulation mechanism needs activation energy ~ 63 kJ mol^{-1}. The value of activation energy demarcates biosorption as physical process and bioaccumulation as chemical process (Kadukova and Vircikova 2005).

Biological removal of zinc by microorganisms

Various research workers (Cabral 1992; Mattuschka and Straube 1993, Mameri et al. 1999; Salehideh and Shojaosadati 2003; Chen et al. 2005) have demonstrated biological removal of zinc mediated by microorganism. Both living and dead microorganisms had been used in past to remove metal from liquid phase (Malik 2004; Liu et al. 2004; Wang and Chen 2009). The bacterial biomass had gained substantial and significant interest in remediation of heavy metals in the series of various biomasses relatively. The rationale behind the supremacy of bacterial cell usage is (1) bacteria are biomass that contribute to the tremendously large fraction of biomass present on earth $\sim 10^8$ g (Mann 1990), they are smaller in size, (2) they have capability to grow in controlled conditions, and (3) they are flexible towards the changing environmental conditions (Urrutia 1997). Usually, dead microorganism binds with the heavy metal ion through physiochemical mechanism. The biosorption can occur with one type of mechanisms or a combination of more than one or more mechanisms. Some of the physicochemical mechanisms are physical adsorption, surface complexion, surface micro precipitation, ion exchange, etc. (Veglio and Beolchini 1997; Chojnacka 2009). Cell wall of the microorganism contains polysaccharide, proteins and lipids (Chojnacka 2009). These cellular entities provide negatively charged functional groups like carboxylate, hydroxyl, sulfate, phosphate and amino groups on the surface of dead microorganism. The negatively charged functional groups on the surface of bacterial cell surface render living bacterial cells with tremendously higher removal capacity of metal ion from liquid phase (Wakatsuki 1995; Kazy et al. 2009; Liu et al. 2004; Wang and Chen 2009; Chatterjee et al. 2010). Figure 1 represents the schematic of non-metabolism-mediated biosorption of heavy metals.

The bioaccumulation of heavy metal ions in living microorganisms is a multistage process. Usually, the multistage of bioaccumulation consists of biosorption followed by intra or extracellular accumulation of metal ions. Figure 2 represents the various routes of bioaccumulation of heavy metal ions.

The cellular structure of living bacterial cell consists of several non-membrane bound units like ribosome, Golgi bodies, endoplasmic reticulum, nucleoid (Non membranous bound structured nucleic acid), cell wall and cell membrane, etc. The broad classification of bacterium

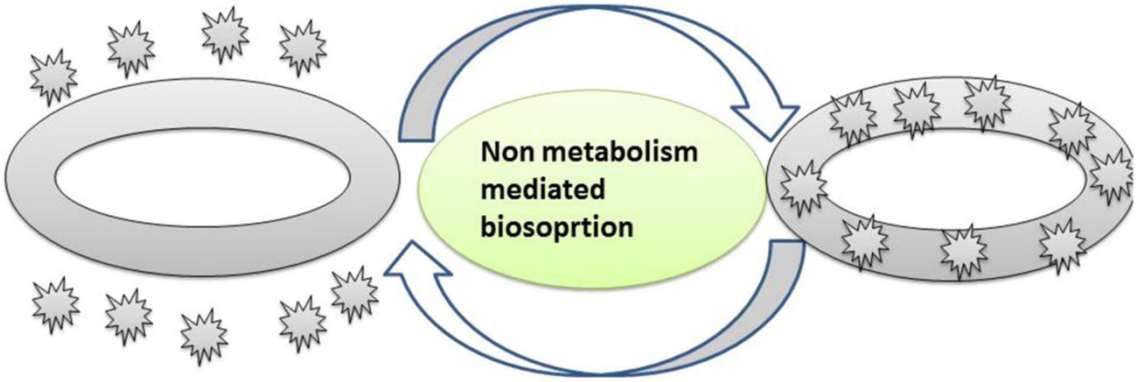
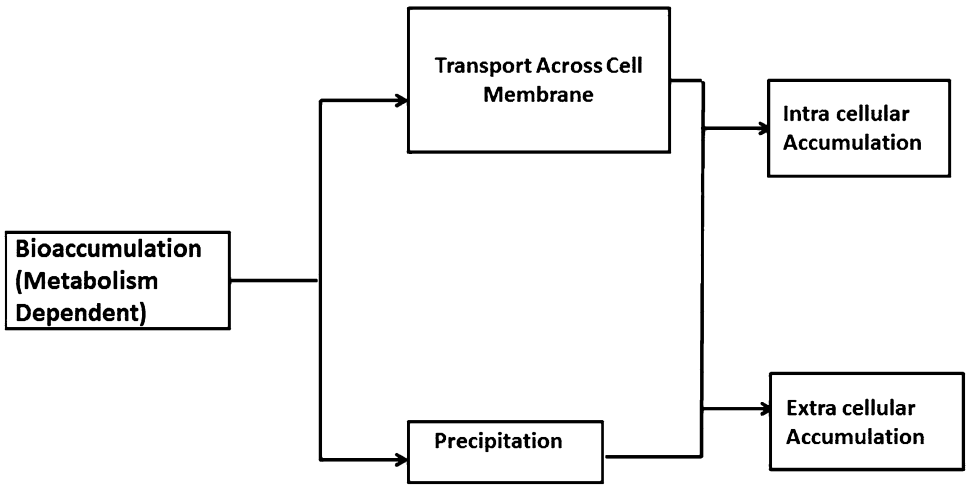


Fig. 1 Non-metabolism-dependent biosorption of heavy metal ions

Fig. 2 Metabolism-dependent biosorption of heavy metal ions



segregates the bacteria into two categories namely Gram positive and Gram negative. Gram-positive bacterium cell wall contains relatively higher percentage of cross-linked peptide-based peptidoglycan. The cross linking of peptides is usually not present in Gram-negative bacterium cell wall. The cross linking of peptides in peptidoglycan matrices results in the development of peptidoglycan sacs. These sacs are quite flexible and molecules can easily fit in these sacs. The peptidoglycan in Gram-positive bacterium contains substantial quantity of polymers of glycerol and ribitol joined by phosphate group. These polymers have unique characteristics of Gram-positive bacterial cell and they are called as teichoic and teichuronic acids, which bind to the peptidoglycan with covalent linkage or get attached with lipids of plasma membrane. Teichoic acids extend themselves to the outer surface of the peptidoglycan, which results in creating a negative charge on the bacterium cell surface. Various researches have proved that teichoic and teichuronic acids have significant role in metal ion binding (Remacle 1990; Urrutia 1997; Moat and Foster 2002; Prescott et al. 2002). Comparatively, the cell wall Gram-negative bacterium is quite complex. The cell wall of the Gram-negative bacterium contains lipopolysaccharides (LPS), proteins and phospholipids. The presence of LPS on the cell wall of Gram-negative bacterium renders the net negative charge on bacterium outer surface. The phosphate and carboxyl groups present in LPS and phospholipids are primary sites of metal ion binding (Remacle 1990; Urrutia 1997; Moat and Foster 2002; Prescott et al. 2002). Other sorts of microorganism repertoire secrete outside their cell wall an acidic slime or capsule. The array of these capsules is an interesting site for metal ion binding (Urrutia 1997; Madigan et al. 2000). Yee and Fein (2001) suggested that the structures giving rise to metal and proton adsorption on the bacterial cell walls are common in almost all the bacterial species involved in metal adsorption. Ozdemir et al. (2009) performed study on the removal of zinc by dead cells of *Goebacillus toebii sub sp. decanicus* and *Goebacillus thermoleovorans sub sp. stromboliensis* in batch stirred system. The authors reported that the stretching of O–H and N–H mediated the metal ion binding on microbial cell surface. The Fourier Transformation Infra Red Spectrum (FTIR) peaks were obtained at 3,315, 1,661, 1,545, 1,403, 2,930 and 2,990 cm^{-1}. These peaks indicated

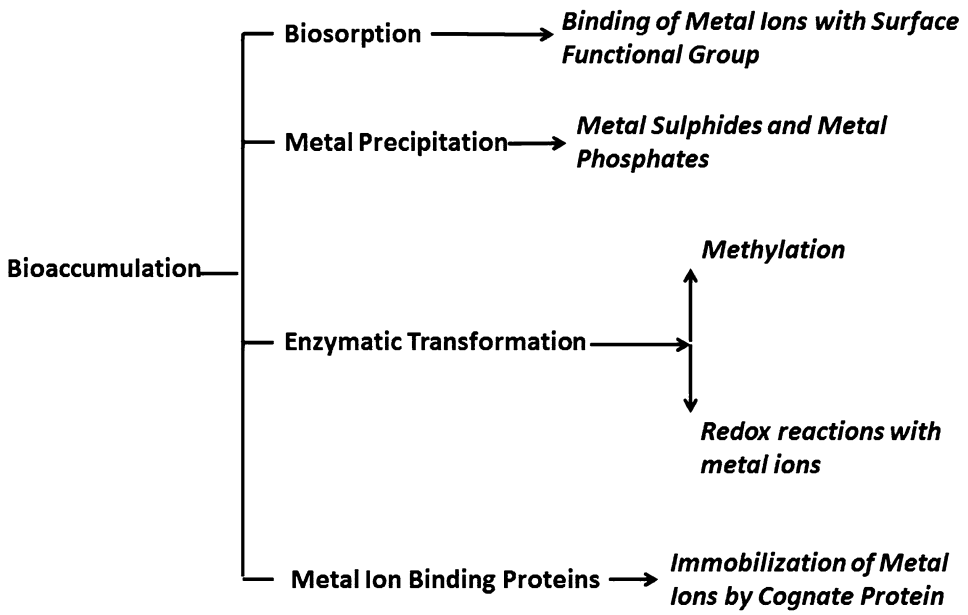


Fig. 3 Various routes of bioaccumulation of heavy metal ions

the involvement of O–H, N–H, –C=O, –C=C, C–H bending in aromatic ring and aliphatic stretching. These groups indicated the involvement of amine, carboxyl and aromatic groups. Silva et al. (2009) reported the biosorption of zinc by *Pseudomonas aeruginosa* AT18.

The dead cells go through cell microaeration process that can break the cell wall making more sites for binding of metal ion. Vullo et al. (2008) used the free and immobilized cells of *Pseudomonas veronii* 2E to remediate the zinc from liquid waste. The authors observed the changes in the negative charge on the cell surface and obtained 50 % removal of zinc in ternary metal ion system. The authors also reported that increase in initial concentration of metal ion led to the decrease in density of negative charges. Esposito et al. (2001) investigated the characterization of biomass (*Sphaerotilus natans*). The authors hypothesized that the two main functional groups namely carboxylic and phosphate group have tremendous potential to bind with metal ion in liquid phase. Choudhaury and Srivastava (2001) studied the detailed mechanism of zinc resistance in bacterium. The study revealed that the zinc-resistant bacterium have series of mechanisms such as metal ion sequestration, active efflux of metal ions, bio-precipitation and changes in the cell wall of the bacterium cell to resist the toxicity of zinc. Either the single mechanism or a combination of these well regulatory mechanisms helps the bacterial cell to retain essential quantity of zinc and to avoid the toxic concentration of zinc to build up inside the cell. Lodi et al. (1998) reproduced the results of biosorption of zinc from liquid phase. The authors reported that under the theory of mass transfer, metal ion biosorption on microbial cell surface was mediated by simple biosorption as well as by the movement of metallic ions inside the cells. Figure 3 represent the various schemes of metal ion bioaccumulation.

Various researches indicate that the uptake of metal ion is a biphasic process. The first step of the process consists of rapid biosorption followed by slower uptake of metal ions inside the cell (bioaccumulation). The metal ions diffuse inside bacterial cell, and associate with intracellular proteins or metal chelators before being captured in vacuoles during the detoxification process of metal ions. Frequently, this process is irreversible and there is less chance of release of metal ions back into the environment (Gekeler et al. 1988). Apart from adsorption on the cell wall, metal resistance has been reported in a wide range of Gram-negative as well as Gram-positive bacteria, many of which have been reported to have a resistance against several different toxic heavy metals. This kind of resistance also comes from genes located within the bacterial genome or plasmids such as pMOL 28 or pMOL 30 (Siddiqui et al. 1989; Liesegang et al. 1993; Mergeay et al. 2003). The zinc resistance is harbored by the *czc* operon. Table 5 enlists the biosorption capacities of various living and non-living microorganisms with respect to zinc ions.

The uptake capacities of various microorganisms cited above have been derived in various environmental conditions; however, still their tabulation provides a very peer analysis of metal uptake by bacterium strains in various physiological states. As mentioned earlier, the uptake of heavy metals by non-living bacterial biomass is accomplished by physico-chemical interactions. Contrary to this, uptake of heavy metal by living biomass (bioaccumulation) is the result of bacterial cell resistance towards the heavy metal ions. Three independent mechanisms operate in case of bioaccumulation. They are as follows: (1) efflux of

Table 5 Tabulation of uptake capacities of various living and non-living microorganism in terms of zinc uptake

Name of biomass	Physiological stage	Initial metal ion conc. (mg l^{-1})	pH	Temp. (°C)	Uptake capacity (mg g^{-1})	Percentage removal	References
Pseudomonas putida	Inactive	1,000	7.0–7.5	ND	6.9	80	Pardo et al. (2003)
Streptomyces rimosus	Inactive	100	7.5	20	30	ND	Mameri et al. (1999)
Bacillus firmus	Polysaccharide (inactive)	0–500	6	25	418	61.8	Salehideh and Shojaosadati (2003)
Bacillus firmus	Polysaccharide (inactive)	0–2,000	6	25	722	61.8	Salehideh and Shojaosadati (2003)
Pseudomonas veronii 2E	Living	32,690	7.5	32	ND	50	Vullo et al. (2008)
Biological sludge	Aerobic (Living)	450	5–6, uncontrolled	20 ± 1	138.30	18.1	Artola and Rigola (1992)
	Thickened (living)	313.20	5–6, uncontrolled	20 ± 1	28.39	32.7	Artola and Rigola (1992)
	Anaerobic (living)	455.50	5–6, uncontrolled	20 ± 1	38.38	27.5	Artola and Rigola (1992)
	Dewatered (inactive)	312.50	5–6, uncontrolled	20 ± 1	33.87	43.4	Artola and Rigola (1992)
	Dehydrated (inactive)	312.50	5–6, uncontrolled	20 ± 1	12.15	16.6	Artola and Rigola (1992)
Pseudomonas putida CZ1	Living	6.5–279.4	5	30	24.4 ± 0.5	ND	Chen et al. (2005)
Pseudomonas putida CZ1	Inactive	6.5–279.4	5	30	14.4 ± 0.81	ND	Chen et al. (2005)
Pseudomonas putida strain B14	Living	65,380	7	5	ND	80	Andreoni et al. (2003)
Bacillus circulans strain EB 1	Living	ND	7	37	22 (mg l^{-1}) Not defined in terms of mg g^{-1}	68	Yilmaz (2003)
Bacterial strain W-6	Living	100	6	40	27.63 (mg l^{-1}) Not defined in terms of mg g^{-1}	81.68	Yaman and Zia (2010)
Brevibacterium sp. strain HZM-1	Living	0–653,800	3	30	42	ND	Taniguchi et al. (2000)
Aphanothece halophytica	Living	0–47.9	6.5	30	133	–	Incharoensakdi and Kitjaharn (2002)
Streptoverticillium cinnamoneum	Living	65.38–114,415	6.5	28 ± 3	22.7 ± 0.9	100	Puranik and Panikar (1999)
Streptoverticillium cinnamoneum	Chemically or physically pretreated cell (Inactive)	65.38–114,415	6.5	28 ± 3	6.9–24.8	reduced by 22–78 %	Puranik and Panikar (1999)
Streptomyces rimosus	Chemically pretreated (inactive)	100	7.5	20	80	ND	Mameri et al. (1999)
Thiobacillus ferrooxidans	Inactive	100	6	25	82.61	ND	Celaya et al. (2000)
Thiobacillus ferrooxidans	Chemically pretreated (living)	25–150	6	40	172.4	ND	Liu et al. (2004)
Pseudomonas\ syringae	Living	0–13	ND	22	8	ND	Cabral (1992)

Table 5 continued

Name of biomass	Physiological stage	Initial metal ion conc. (mg l^{-1})	pH	Temp. (°C)	Uptake capacity (mg g^{-1})	Percentage removal	References
Streptomyces noursei	Living	0.6–65	5.8	30	1.6	ND	Mattuschka and Straube (1993)
Geobacillus thermoleovorans sub.sp. *stromboliensis* (G2)	Inactive	10–300	4	70	29	ND	Ozdemir et al. (2009)
Geobacillus toebii sub.sp. *decanicus* (G1)	Inactive	10–300	5	80	21.1	ND	Ozdemir et al. (2009)
Geobacillus thermodentrificans	Inactive	88	5	65 ± 1	42.9	9.02–55.14	Chatterjee et al. (2010)
Pseudomonas aeruginosa AT 18	Living	70	7	30	77.5	87.7	Silva et al. (2009)
Sphaerotilus natans	Living	3.6–901.4	6.0–7.5	30	3.4–741.4	ND	Lodi et al. (1998)
Zinc sequestering bacterium VMSDCM Accession no. HQ108109	Inactive	ND	7	35	13,720	100	Mishra et al. (2011a, b, c)

ND = Not defined

metal ion by permeability and active transport, (2) intra cellular physical and extracellular sequestration (by metallothionein protein), and (3) detoxification (mediated by redox reactions). Since zinc ion occurs exclusively occurs in its divalent stage with the completely filled *d* orbital; therefore, the possibility of zinc ion to undergo redox reaction is quite scarce. The resistance mechanisms in bacterium cells against higher zinc concentration, such as metal ion efflux, extracellular and intracellular accumulation and sequestration, are of particular interest. These resistances are conferred to the bacterium cell by the set of genes or operon. The most widely studied operon system in bacterial cell meant for resistance against the metal ions is *czc* operon of plasmid pMOL 30 in case of *Ralstonia eutropha* strain CH34. This operon system encodes for three structural genes namely czcC, czcB and czcA. These genes impart resistance to the bacterium cell against zinc. The products of structural genes result in complex cation efflux pump (Choudhaury and Srivastava 2001).

Biological removal of zinc by algae and fungi

Among the various groups of the biosorbents used in recent years, algae have acquired a worthy position in biosorption of heavy metal ions from liquid phase (Klimmek and Stan 2001; Davis et al. 2003; Romera et al. 2007; Lesmana et al. 2009). Recent studies in the field of biosorption of heavy metals have focused on brown, green and red algae (Holan et al. 1993; Holan and Volesky 1994; Matheickal and Yu 1999; Davis et al. 2003). Algae come under the plant kingdom, diverging from unicellular structure to multicellular organism, with their habitats ranging from fresh water to marine water and from snow to exposed rock. The algae kingdom is not homogeneous and, therefore, Bold and Wynne (1985) proposed the classification of algae group on the basis of their storage products and cell wall composition. There classification includes *Cyanophyta* (blue green algae*), Prochlorophyta, Pheaophyta, Chlorophyta* (green algae), *Chromophyta* (brown algae), *Rhodophyta* (Red algae), *Charophyta*, *Euglenophyta*, *Pyrrophyta* and *Cryptophyta*. The biosorption of metal ion on the surface of algae depends on the chemistry of cell wall. Various types of mechanisms such as electrostatic attraction, ion exchange, complexion, etc. get involved in metal ion binding. Majority of the algal species contain embedded amorphous and non-crystalline polysaccharides matrix. According to the classification of species, the algae contain xylan, mannan, alginate with fucoidan polysaccharide and sulfated galactans. These groups have tremendous capacity of metal ion binding on the surface of the algal cell wall. The carboxyl, hydroxyl, sulfate, sulfonic acid amino acid in the polysaccharide matrix of the algal cell wall provide the key predominant sites for the biosorption of heavy metal ions. Usually, seaweeds contain high quantity of carboxyl, hydroxyl, phosphate and amine. These groups significantly improve the efficiency biosorption of seaweeds. The authors studied various isotherms, kinetic and mechanistic models for the data obtained at the attainment of equilibrium. Among the various isotherms, kinetic and mechanistic models, Langmuir, pseudo second-order and intraparticle model were found more suitable to interpret the biosorption of ions on *Gymnogongrus torulosus* surface. The authors concluded that the biosorption of zinc and copper is highly dependent on pH and the maximum

removal of zinc and copper was obtained above pH 7. However, the biosorption of lead has shown a little dependency on pH variation. Biosorption of zinc ion on the surface of macro alga *Chaetomorpha linum* was performed by Ajjabi and Chouba (2009). The maximum adsorption of both the heavy metal ions was reported at pH 5. There was a sharp decline in biosorption of zinc ion in liquid phase above pH 5. The decrease in biosorption of zinc ion with the increase in pH from 5 to 7 was due to the formation of anionic hydroxide complexes and their competition with active sites. However, at lower pH values, the concentration of hydrogen ions was significantly higher which poses extreme competition between hydrogen ions and heavy metals for active binding sites resulting in lowering of biosorption of heavy metal ions. The surface characterization of *Chaetomorpha linum* with the help of FTIR spectrum showed the presence of O–H, C–O, N–H, N–H, C–N, N–H, S=O and P–O stretching. The shift in the FTIR vibration showed that the binding of metal ion on the surface of *Chaetomorpha linum* was mediated by these negatively charged functional groups. Biosorption of zinc on the surface of six different types of algae (*Codium vermilaria*, *Spirogyra insignis, Asparagopsis armata, Chondrus crispus, Fucus spiralis and Ascophyllum nodosum*) was performed by Romera et al. (2007). The authors reported that the maximum sorption of various heavy metals was at pH 5 and 6. The authors also concluded that efficiency of six strains of algae in terms of bioremoval of heavy metal ions was more effective compared to bacteria and fungi. Chromophyta, a potential biosorbent contains very significant quantity of alginate and fucoidan in their cell wall. Cellular structures, storage polysaccharides, intracellular and extracellular polysaccharide together with alginate and fucoidan provide tremendous opportunities for the binding of heavy metal ion from liquid phase. On the other hand, *Rhodophyta* and *Chlorophyta* contain *cellulose*, sulfated polysaccharides, agar, carragenates, glycoprotein, etc. for the binding of heavy metal ion from liquid phase. These entities provide negatively charged functional groups for the biosorption of heavy metal ions (Davis et al. 2003; Romera et al. 2007; Lesmana et al. 2009). Table 6 represents the comparative analysis of various algae in terms of their zinc ion uptake capacities. The uptake capacities represented in Table 6 would have been derived in different environmental conditions, yet their simultaneous application provides a substantially significant information and comparison of removal capacities of various algal species in terms of zinc ion from liquid phase. Fungus, another broad category of biosorbent, has been used in various research investigations for biosorption of heavy meal ions from liquid phase (Sharma et al. 2002; Faryal et al. 2006; Ali and Hashem 2007). Some of the genuses of fungi used in various researches are *Streptomyces, Rhizopus, Aspergillus, Penicillin, Saccharomyces, Mucor* (Mameri et al. 1999; Kapoor and Viraraghavan 1995). Majority of these fungal genera are involved in brewery, baking industry, production of enzymes, organic acids like pectinase, acidic lipase, gluconic and citric acid, respectively. *Aspergillus niger* is also involved in biotransformation of ferulic acid, diperpenoid, etc. Yang et al. (2009) reported the biosorption of zinc from liquid waste on the surface of *Aspergillus niger*. Yang et al. (2009) concluded that there was an increase in biosorption efficiency of *Aspergillus niger* with the increase of pH from 3 to 6.5. The modeling of the data obtained at equilibrium of sorption of metal ion showed that pseudo kinetic first-order model and Langmuir isotherm model were found suitable to interpret the kinetics and mechanism of biosorption of metal ion on *Aspergillus niger* surface.

Bayramoglu et al. (2003) attempted the biosorption of zinc on the surface *Trametes versicolor* immobilized on CMC beads. The biosorption of zinc on immobilized *Trametes versicolor* was found to be maximum between pH 4.0 to 6.0. The maximum uptake capacity reported for immobilized living fungal cell was 1.11 mmol g^{-1} of biomass for zinc ions, respectively. Mameri et al. (1999) used the non-living *Streptomyces rimosus* biomass derived from antibiotic fermentation industry for the biosorption of zinc ion in liquid phase. Furthermore, the pretreatment of biomass was performed by NaOH (1 mol l^{-1}). Usage of pretreated biomass in biosorption of zinc ion in liquid phase showed an enhanced efficiency of biosorption. The two types of the biomasses differed in their surface functional groups. The crude biomass showed the FTIR peaks for carboxyl and amina stretching, whereas in the pretreated biomass these two bands were absent. Authors also reported the variation in pH in case of crude biomass. There was no change in pH during biosorption of zinc ion in case of pretreated biomass. These results indicated that preferential mode of biosorption was ion exchange. Zinc biomass exchanged with the H^+ ion in case of crude biomass and in pretreated biomass, the ion exchange occurred between zinc ion and Na ion.

The cell wall of the fungus consists of polysaccharides, lipids, protein, phosphates and inorganic matter. Polysaccharide fraction of fungal cell wall is significantly higher, about 80–90 %. Chitin, nitrogen containing N-acetylglucosamine flexible polysaccharide, makes two layers of cell wall. Inner thick layer of chitin is present in parallel fashion. The cell membrane of fungi is made up of phospholipids and cholesterol, i.e., sterol. Usual type of widely accepted structure of cell membrane is fluid mosaic model with

Table 6 Comparative analysis of various algae in terms of their Zn ion uptake capacities

Name of biomass	Physiological stage	Initial metal ion conc. (mg l^{-1})	pH	Temp. (°C)	Uptake capacity (mg g^{-1})	Percentage removal	References
Chlorella vulgaris	Inactive	100	4	RT	24,190.6	ND	Klimmek and Stan (2001)
L. taylorii	Inactive	100	4–6	RT	32,036.2	ND	Klimmek and Stan (2001)
L. taylorii phos.	Inactive	100	4–6	RT	169,988	ND	Klimmek and Stan (2001)
Ankistrodesmus densus	Inactive	100	4–6	RT	15,037.4	ND	Klimmek and Stan (2001)
Vaucheria dichotoma	Inactive	100	4–6	RT	27,459.6	ND	Klimmek and Stan (2001)
Dunaliella bioculata	Inactive	100	4–6	RT	2,615.2	ND	Klimmek and Stan (2001)
Fucus spiralis, *Laminaria hyperborea, Bifurcaria bifurcata, Sargassum muticum*	Inactive	75–100	4.5	25 °C	18.6–32.0	ND	Freitas et al. (2008)
Sargassum	Inactive	65,380–653,800	5	ND	ND	ND	Figueira et al. (2000)
Sargassum filipendula	Inactive	0–196.14	5	30	41.84	ND	Fagundes et al. (2007)
Caulepra lentilliferra	Inactive	10	1.0–7.5	21 ± 2	1,372.98–2,680.58	ND	Pavasant et al. (2006)
Codium vermilara	Inactive	10–150	6	ND	23.8	ND	Romera et al. (2007)
Spirogyra insignis	Inactive	10–150	6	ND	21.1	ND	Romera et al. (2007)
Asparagopsis armata	Inactive	10–150	6	ND	21.6	ND	Romera et al. (2007)
Chondrus crispus	Inactive	10–150	6	ND	45.7	ND	Romera et al. (2007)
Ascophyllum nodosum	Inactive	10–150	6	ND	42.0	ND	Romera et al. (2007)
Fucas spiralis	Inactive	10–150	6	ND	53.2	ND	Romera et al. (2007)
Laminaria japonica	Inactive	326,900	4.5	RT	91,532	ND	Fourest and Volesky (1997)
Sargassum fluitans	Inactive	326,900	4.5	RT	77,148.4	ND	Fourest and Volesky (1997)
Fucus vesiculosus	Inactive	326,900	4.5	RT	52,304	ND	Fourest and Volesky (1997)

outward and inward projection of polar heads and non-polar heads with several embedded globular proteins. The cell wall of the fungi contains the negatively charged groups, such as carboxyl, hydroxyl, amine, sulfhydryl and phosphate. These negatively charged functional groups involve themselves in biosorption of metal ions. The biosorption of metal ions primarily on fungal cell wall is mediated by ion exchange and complexion. The intracellular uptake and detoxification of metal ions by fungi are due to the presence of metallothioneins, metal excess pool, internal storage and metal sequestration by heat stable proteins. Table 7 represents the uptake capacities of various fungal biomasses in terms of zinc ion uptake. Table 7 summarizes some of the significant results in the field of biosorption by fungal biomass. The biosorption of heavy metal ion mediated by fungal species depends on various factors like pH, temperature, metal ion concentration and biomass concentration (Arica et al. 2003). Iqbal and Edyvean (2004) and Li et al. (2010) have reported the effect of these parameters on sorption of zinc ion on the surface of fungal mass. The data represented in Table 7 have been derived in different environmental parameters, yet comparative analysis among these biomasses provides a fruitful opinion regarding the uptake efficiency of various fungal biomasses.

Table 7 Comparative analysis of various fungal biomasses in terms of their Zn ion uptake capacities

Name of biomass	Physiological stage	Initial metal ion conc. (mg l^{-1})	pH	Temp (°C)	Uptake capacity (mg g^{-1})	Percentage removal	Reference
Streptomyces rimosus	Inactive	100	7.5	20	30	ND	Mameri et al. (1999)
Streptomyces rimosus	Inactive	100	6.5	20	80	ND	Mameri et al. (1999)
Penicillium spinulosum (non growing cell)	Living	2.5	ND	ND	1.3	ND	Kapoor and Viraraghavan (1995)
Penicillium spinulosum (growing cell)	Living	2.5	ND	ND	0.2	ND	Kapoor and Viraraghavan (1995)
Penicillium notatum	Living	ND	7	25	23	2.3 ± 1.6	Siegel et al. (1983)
Rhizopus arrhizus	Inactive	ND	4	25	20	ND	Tobin et al. (1984)
Saccharomyces cerevisae (Portuguese origin)	Inactive	40.8	5.5	ND	3.45	9	Bakkaloglu et al. (1998)
Saccharomyces cerevisae (UK)	Inactive	40.8	5.5	ND	1.95	5	Bakkaloglu et al. (1998)
Penicillium chrysogenum	Inactive	45.5	5.5	ND	19.2	42	Bakkaloglu et al. (1998)
Saccharomyces cerevisae	Living Free cells	ND	5	25	23.41 ± 0.13	ND	Al Saraj et al. (1999)
Phanerochaete chrysogenum	Living (immobilized cells)	100	6	20 ± 2	41.9	ND	Iqbal and Edyvean (2004)
Phanerochaete chrysogenum	Living (free cells)	100	6	20 ± 2	34.13 ± 1.84	ND	Iqbal and Edyvean (2004)
Aspergillus niger	Living	64.8	6.5	30	2.82	ND	Yang et al. (2009)
Trametes versicolor (immobilized)	Living	400	4–6	15–45	86,955.4	ND	Bayramoglu et al. (2003)
Trametes versicolor	Inactive	400	4–6	15–45	109,184.6	ND	Bayramoglu et al. (2003)
Phanerochaete chrysosporium (immobilized cells)	Living	30–600	6	15–45	37	ND	Arica et al. (2003)
Phanerochaete chrysosporium	Inactive	30–600	6	15–45	48	ND	Arica et al. (2003)
Mucor rouxii	Living	10	5	ND	7.75	ND	Yan and Viraraghavan (2003)
Mucor rouxii	Inactive	10	6	ND	53.85	ND	Yan and Viraraghavan (2003)
Penicillium chrysogenum PE-10/94	Inactive	65.38–65,380	7	21 ± 1	13	32	Skowronski et al. (2001)
Saprolegnia delica	Living	0.003	8	20	ND	44	Ali and Hashem (2007)
Trichoderma viride	Living	0.003	6	25	ND	61.7	Ali and Hashem (2007)
Fungal biomass isolated from industrial wastewater	Living	500	4.5	30	77	ND	Sharma et al. (2002)
Streptomyces ciscaucasicus	Living	1–150	5.0	28	42.75	ND	Li et al. (2010)
Streptomyces ciscaucasicus	Inactive	1–150	5.0	28	54	ND	Li et al. (2010)

Biological removal of zinc by various agricultural waste, resins, clay and industrial byproduct

As mentioned earlier, the important characteristics of biosorption method include the eco-friendly nature, cost effectiveness and availability of abundance. The agricultural waste makes a very diverse category of non-living biomasses, which are readily available to be used as biosorbent for heavy metal ions. The biosorption efficiency or uptake capacity of these biomasses depends on many

factors like particle size, surface morphology, functional groups present on the surface of the biomass, porosity, surface area, pH, temperature, initial concentration of metal ions, etc. (Sheha 2007; Rocha et al. 2008; Arshad et al. 2008; Agorboude and Navia 2009). The industrial byproducts and clays are also readily available (Vengris et al. 2001; Srivastava et al. 2007), to be used as biosorbent for metal ion removal from liquid phase. Resins, certainly ion exchange resins, are quite expensive, hence there usage is not a cost effective option for biosorption of heavy metal ion.

Mishra et al. (2010, 2011a, b, c) carried out the investigation on biosorption of zinc ion on various sorts of biosorbents, such as jack fruit peel, pine apple peel, mango bark sawdust, *Cedrus deodara* sawdust, *Zinc sequestering bacterium VMSDCM* Accession no. HQ108109 (Accession number is provided by National Center for Biotechnology Information-NCBI, US) and eucalyptus leaf powder. The investigations evidenced the fact that the surfaces of these biosorbents were quite porous and quite enriched with negatively charged functional groups.

Tofan et al. (2008) used the thermal power plant ash for the biosorption of zinc ion in liquid phase. Authors obtained thermal fly ash as byproduct of thermal power plant. Langmuir isotherm model was studied to evaluate the data obtained at the attainment of equilibrium. The monolayer sorption capacities obtained through Langmuir model were 5.75 mg g^{-1} for zinc. Dynamic modeling of the data showed that the Lagergren pseudo first order model had been more suitable to interpret the sorption of zinc ions on the ash of thermal power plant in liquid phase.

Naiya et al. (2008) performed the biosorption of zinc ions by sawdust and neem bark in liquid solution. The optimum pH for the biosorption of zinc ion was 5. Dynamic modeling of the data represented the pseudo second-order model to interpret the kinetics of sorption of zinc ions. The isotherm modeling of data showed equal inclination towards both Langmuir and Freundlich isotherms. The research also evidenced the presence of various negatively charged functional groups such as carboxylic acid, amino, amine, amide and sulfonated groups on the surface of sawdust and neem bark before the adsorption of metal ions.

Mishra et al. (2012a, b) performed the studies on biosorption of zinc ions on the surface of immobilized bacterium cells in packed bed column. In the sidelines of the work, the authors performed the studies on hydrodynamic parameters of the packed bed column. The authors reported that by decreasing the flow rate (ml h^{-1}) of effluent in the column, residence time of the pollutant can be increased in the column, which in turn results in higher removal of metal ions from the effluent. However, the authors also mentioned that particle size below 0.5 mm is not suitable for column, as <0.5 mm because the chances of huge pressure drop increase very rapidly.

Cesur and Balkaya (2007) performed the biosorption of zinc ion using and industrial byproduct phosphogypsum. Freundlich isotherm was found suitable to interpret the sorption of zinc ion on phosphogypsum. The maximum adsorption of zinc was obtained between pH 9 and 10. The uptake capacity of 2.57 mg g^{-1} of biomass was reported. The adsorption equilibrium was reached in 40 min.

Biosorption of zinc by rice straw was attempted by Rocha et al. (2008). The authors reported that the biosorption of metal ions was exothermic in nature. The maximum adsorption of metal ion was obtained at pH 5 and at 25 ± 1 °C. The characterization of the rice straw showed the presence of O–H stretching, C–H stretching, C=C stretching, Si–O stretching and Si–O bending on the surface of rice straw. The Freundlich isotherm parameter analysis showed the preferential trend of sorption of metal ions as Cd (II) > Cu (II) > Zn (II) > Hg(II). The equilibrium was obtained in 1.5 h.

Table 8 represents the comprehensive view of uptake capacities of various biosorbents in terms of zinc ion uptake. Most of the studies on biosorption of heavy metals and increasing repertoire of publication have focused on single metal ion system and on multi metal ion system. Similarly, Table 8 has dealt with the uptake capacities of various biosorbents derived in different environment conditions. Table 8 provides a deep insight into peer comparative analysis of uptake capacities of a range of biosorbents.

Biosorption isotherms, kinetics and mechanisms

Isotherm modeling of the data obtained at the attainment of the equilibrium in batch or continuous biosorption studies is a very imperative concept to elucidate the partition of metal ions between solid and liquid phase. Most of the studies in biosorption of heavy metals have peer reviewed the isotherm modeling of the metal ion binding in liquid phase (Hanif et al. 2007; Mishra et al. 2010, 2011a, b, c, 2012a, b). In the present investigation, various types of isotherm models have been discussed in the next upcoming sections.

Langmuir model This is a widely used model in the study of adsorption of metal ion on the surface of adsorbent. Mishra et al. (2010, 2011a, b, c) used Langmuir isotherm to elucidate the biosorption of zinc ion on the surface of *Cedrus deodara* sawdust and eucalyptus leaf powder. The authors reported that Langmuir isotherm has suitability in explaining the biosorption of zinc on the surface of *Cedrus deodara sawdust* and eucalyptus leaf powder.

However, Sengil and Ozacar (2009) reported the lower goodness of fit for Langmuir isotherm in terms of

Table 8 Comparative analysis of uptake capacities of various adsorbents/biosorbents in terms of Zn ion uptake

Name of biomass	pH	Temp. (°C)	Initial concentration of Zn (II) ion (mg l^{-1})	Contact time (h)	Uptake capacity (mg g^{-1})	Functional groups/ compounds available	References
Bagasse fly ash (BFA)	6	20–50	3,269,000–32,690,000	5	24,190.6–25,498.2	Si–OH, adsorbed water, OH CH_2, C=O, CHO, aromatic CH, carboxyl carbonate structures	Srivastava et al. (2007)
Rice husk ash (RHA)	6	20–50	3,269,000–32,690,000	5	15,037.4–16,998.8	Free and hydrogen bonded OH group, C=O, CHO, aromatic CH, carboxyl carbonate structures	Srivastava et al. (2007)
Modified clay sorbent	5	20 ± 1	10–2,000	6	68,322.1	Hydromica, quartz and feldspar, iron and aluminum hydroxide	Vengris et al. (2001)
Valonia tannin resin	5	ND	5–100	ND	35.51	Phenolic, hydroxyl and oxyl groups	Sengil and ozacar (2009)
Zeolite NAY	4.5	30	3.26–98.07	15	47.40–53.93	3D framework of silica and alumina joined by shared oxygen atom	Ostroski et al. (2009)
Pinus sylvestris L.	6	35	10–100	<1	15.12	Lignin, tannin, rosin, cellulose	Ucun et al. (2009)
Ion exchange resin	5.5	25 ± 2	ND	72	176,526	H^+, Ca^{2+}, Na^+	Shek et al. (2009)
Neem leaves	4	25	25–800	12	147.08	ND	Arshad et al. (2008)
Neem stem bark	5	25	25–800	12	137.67	ND	Arshad et al. (2008)
Brine sediment	7	25	75	11.5	4.85	Halite, calcite, quartz, iron siliceous, calcium oxide, Ca, Fe	Agorboude and Navia (2009)
Sawdust	7	25	75	11.5	2.58	Calcium, magnesium, sodium, potassium	Agorboude and Navia (2009)
Combination of brine sediment and sawdust	7	25	75	11.5	5.59	CH, C–O, C–C, alcoholic and phenolic group	Agorboude and Navia (2009)
Triticum aestivum	ND	ND	ND	ND	ND	ND	
Triticum aestivum	6.5	RT	ND	ND	15,691.2	ND	Dupont et al. (2005)
Activated carbon, Kaolin, bentonite, blast furnace slag and fly ash	6	25 ± 2	50–100	3	3.05–11.24	ND	Mohan and Singh (2002)
Activated from bagasse	4.5	25 ± 1	200	10–12	31.11	ND	Mohan and Singh (2002)
Phosphogypsum	9.0–110	RT	0.1–100	0.66	2.57	ND	Cesur and Balkaya (2007)
Thermal power plant	4.5–5	18	30–130	0.25–24	5.75	ND	Tofan et al. (2008)
Tectona grandis L. F	5	30–60	20–100	3	16.42	ND	Kumar et al. (2006)
Esterified lemon	4.8	25–55	65,380–1,634,500	0.5–4	5,264–62,764.8	ND	Arslanoglu et al. (2008)
Amberlite IR-20 synthetic resin	4–8	1.5	ND	3	50,022,238	$–SO_3H$	Demirbas et al. (2005)
Biosolids	4	20 ± 2	4,968.8–98,070	5	36,874.32	ND	Norton et al. (2004)

Table 8 continued

Name of biomass	pH	Temp. (°C)	Initial concentration of Zn (II) ion (mg l^{-1})	Contact time (h)	Uptake capacity (mg g^{-1})	Functional groups/ compounds available	References
Rice straw	5	25 ± 1	189,602–2,007,166	1.5	8,630.16	Hydroxyl, C–H stretching, C=C in aromatic ring, Si–O stretching and Si–O bending	Rocha et al. (2008)
Calcium hydroxyapatite	2–8	30 ± 1	60–120	3	102.04	OH group, CO_3^{2-}, PO_4^{3-}	Sheha (2007)
Barium hydroxyapatite	2–8	30 ± 1	60–120	3	36.62	OH group, CO_3^{2-}, PO_4^{3-}	Sheha (2007)
Short hemp fibers(Chemically modified)	5.5	RT	3,269–13,076	0.05–2	5,099.64	ND	Pejic et al. (2008)
Sawdust	5	30 ± 2	25	3	14.10	Carboxylic, amine, amide, sulfonate, amino	Naiya et al. (2009)
Neem bark	5	30 ± 2	25	3	13.29	Carboxylic, amine, amide, sulfonate, amino	Naiya et al. (2009)
Eucalyptus leaf powder	5	20 ± 1	100	6	23.5	Carboxylic, amine, amide, hydroxyl, methyl	Mishra et al. (2010)
Cedrus deodara sawdust	5	45	100	2.5	97.39	Carboxyl, hydroxyl, amine, amide methyl	Mishra et al. (2011a, b, c)

biosorption of zinc on valonia tannin resin against Freundlich isotherm.

Demirbas et al. (2005) performed the sorption of zinc in liquid phase on the surface of Amberlite IR-120. The work evidenced that the goodness of fit of the isotherm for Langmuir model for zinc ion was quite less compared to Freundlich model. The model assumes that the sorption of metal ions occurs in monolayer coverage of biosorbent surface, all active sites are same and symmetrical (homogeneous surface), adsorbate binding is independent of adjacent site occupancy, single site is occupied by singe adsorbate particle and rate of adsorption is equal rate of desorption (dynamic isotherm). The linear model of Langmuir isotherm has been shown in Eq. 1.

$$\frac{C_e}{q_e} = \frac{1}{K_l q_{max}} + \frac{C_e}{q_{max}} \quad (1)$$

q_{max} and K_l are the maximum uptake capacity (mg g^{-1}) and Langmuir constant or sorption equilibrium constant (l mg^{-1}), respectively. The value of q_{max} and K_l can be calculated from the slope and intercept of plot extrapolated between C_e/q_e and C_e. The other linear forms of the Langmuir equation have been shown in Eqs. (2–5) (Nemr 2009; Febrianto et al. 2009)

$$q_e = \frac{q_{max}(bC_e)}{1 + bC_e} \quad (2)$$

$$\frac{1}{q_e} = \left(\frac{1}{bq_m}\right)\frac{1}{C_e} + \frac{1}{q_m} \quad (3)$$

$$q_e = q_m - \left(\frac{1}{b}\right)\left(\frac{q_e}{C_e}\right) \quad (4)$$

$$\frac{q_e}{C_e} = bq_m - K_L q_e. \quad (5)$$

In the Langmuir model, the saturation capacity of the adsorbent (q_{max}) is equal to the saturation of the identical sites. The Langmuir constant b has special relationship with temperature. The increase or decrease in the value of b with the increase of temperature explains the thermodynamic feasibility of the biosorption mechanism as endothermic or exothermic (Ho and Ofomaja 2006; Shaker 2007; Vilar et al. 2007; Padmavathy 2008).

Freundlich model Yang et al. (2009) evaluated Freundlich and Langmuir isotherm models to study the biosorption of zinc ions on the surface of *Aspergillus niger*. The study was conducted in the presence of aluminum, iron and lead. The findings of the investigation showed that the Langmuir model with high R^2 was found more suitable to interpret the biosorption of zinc ion on the surface of *Aspergillus niger*.

Biosorption of zinc ions in liquid phase on the surface of phosphogypsum was performed by Cesur and Balkaya (2007). The authors presented both the linear and non-linear Langmuir and Freundlich isotherms and used both isotherm models to fit the data obtained at the attainment of equilibrium. Freundlich model was found superior to interpret the sorption of zinc ions in liquid phase between

both the models. Demirbas et al. (2005) used Freundlich isotherm to effectively interpret the sorption of zinc ions on the surface of Amberlite IR-120.

Freundlich isotherm is an empirical relationship between equilibrium concentration of metal ion in liquid phase and solid phase. The assumptions of Freundlich model are as follows:

1. Adsorbent surface is heterogeneous and
2. Multilayer adsorbent surface coverage is done by adsorbate

Nonlinear exponential form of Freundlich equation has been represented in Eq. (6)

$$q_e = K_f C_e^{\frac{1}{n}}. \quad (6)$$

Linear form of Freundlich model can be represented as follows:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (7)$$

K_f and $1/n$ are Freundlich constant (mg g^{-1}) and parameter for surface heterogeneity (Febrianto et al. 2009). Freundlich isotherm is unable to predict metal ion sorption equilibrium condition at extreme conditions. In other words, the Freundlich model works from very low range of concentration gradient of adsorbate ion to intermediate concentration. (Liu and Liu 2008; Febrianto et al. 2009).

Temkin model Very scarce research has been made on the applicability of Temkin model in biosorption of heavy metals from liquid phase. Mishra et al. (2011a, b, c) performed the isotherm modeling of zinc ion in liquid phase on the surface of *Cedrus deodar* sawdust. The authors evidenced the fact that the sorption of zinc ion on the surface of *Cedrus deodar* sawdust followed the Temkin model at 318 K. The authors also showed the value of model constants B_t and ln K_t. The model constants were calculated as slope and intercept of the isotherm model.

Temkin isotherm assumes the temperature-dependent linear decrease in heat of sorption. The relation has been represented in Eq. (8) (Febrianto et al. 2009)

$$q_e = B_t \ln(K_t C_e) \quad (8)$$

where B_t constant related to the heat of adsorption and K_t (l g^{-1}) are model constants. Usually, this model is used to explain the sorption of metal ion on heterogeneous surface.

Dubinin–Radushkevich (D–R) model Naiya et al. (2008) applied Dubinin–Radushkevich isotherm for the curve fitting of the data obtained at the attainment of equilibrium. The authors reported very high value of correlation coefficient (r^2). The value of correlation coefficient indicated the suitability of Dubinin–Radushkevich isotherm to explain the biosorption of zinc in liquid phase on the surface of sawdust and neem bark. The authors also used the model parameters to evaluate the mean biosorption energy and it was found that biosorption of zinc on the surface of sawdust, and neem bark was mediated by physical adsorption.

Sari and Tuzen (2008) used this isotherm to evaluate the biosorption of total chromium on the surface of red algae *Ceramium virgatum*. The investigation concluded the fact that Dubinin–Radushkevich model was suitable for explaining the biosorption of total chromium in liquid waste on the surface of *Ceramium virgatum*. With the help of Dubinin–Radushkevich, the mean biosorption energy was calculated and it was found to be 9.7 KJ mol^{-1}. The value of mean biosorption energy calculated through Dubinin–Radushkevich isotherm indicated that chemisorptions were the main mechanism of metal ion sorption on the surface of *Ceramium virgatum*.

This model assumes the heterogeneous surface characteristic of the adsorbent. The model equation has been shown in Eq. (9) (Sari and Tuzen 2009).

$$q_e = q_{max} \exp \frac{\left[\left(-RT \ln\left(\frac{C_e}{C_s}\right)^2\right)\right]}{\beta \varepsilon^2} \quad (9)$$

where R is gas constant (8.314 J mol^{-1} K^{-1}), T is absolute temperature (K), β is model constant, ε is polanyi potential and C_s is zinc ion solubility at given temperature. The model assumes the sorption of metal ions on energetically non-uniform surface. The model provides the significant explanation of equilibrium data (Igwe and Abia 2007; Cabuk et al. 2007).

Kinetic and mechanistic modeling

Kinetic studies are required to find out the rate and mechanism of reaction coupled with determination of rate-controlling step (Metacaf 2001). The study of kinetic models also helps in the design of continuous adsorption columns. Kinetic studies are required to find out the rate and mechanism of reaction coupled with determination of rate-controlling step Metacaf (2001). The rate model study also helps in the design of continuous adsorption columns (Basha et al. 2009).

Pseudo first order model Pseudo first order model was used by Fan et al. (2008) to elucidate the mechanism of biosorption of zinc ion on the surface of *Penicillium simplicissimum*. The authors represented both non-linear and linear model of pseudo first order model. The constant of the model was obtained as the slope of the linear model. The investigation evidenced that pseudo second-order model with higher correlation coefficient was far more

better to explain the sorption of metal ions on the surface of *Penicillium simplicissimum* against pseudo first order model between 20 and 40 °C. The investigation also concluded that the value of Pseudo first order model constant (K_1) did not vary significantly with the rise of temperature.

This model assumes the presence of physical forces of attraction between adsorbate and adsorbent particles. The binding of adsorbate with adsorbent is reversible and non-dissociative. The model also considers that the rate of binding of adsorbate species with adsorbent particle is directly proportional to the number of vacant active sites present on the surface of adsorbent. The non-linear form of pseudo first order reaction model has been represented in Eq. (10) (Sari and Tuzen 2009)

$$\left[\frac{\mathrm{d}q_t}{\mathrm{d}t}\right] = K_1(q_\mathrm{e} - q_\mathrm{t}) \tag{10}$$

where q_e and q_t are uptake capacities of metal ion per unit of adsorbent at equilibrium and at time t and K_1 is the zinc ion biosorption constant. On integrating the Eq. (4) at boundary conditions $q = 0$ at $t = 0$ and $q = q_\mathrm{t}$ at $t = t$, we get Eq. (11)

$$\log(q_\mathrm{e} - q_\mathrm{t}) = \log q_\mathrm{e} - \frac{K_1 t}{2.303} \tag{11}$$

The slope and intercept of plot between log $(q_\mathrm{e} - q_\mathrm{t})$ and time yield the value of reaction constant K_1 (min^{-1}) and log q_e (mg g^{-1}), respectively. Pseudo first-order reaction model works on the principle of linear driving force (Liu and Liu 2008). Tremendous number of researches on heavy metal bioremediation has focused on the successful application of pseudo first order model (Hanif et al. 2007; Preetha and Viruthagiri 2007; Pamukoglu and Kargi 2007).

Pseudo second-order model Mishra et al. (2010, 2011a, b, c) performed the study of biosorption of zinc ion in liquid phase on the surface of the *Cedrus deodara* sawdust and *Eucalyptus leaf* powder. The investigation revealed the fact that the sorption of zinc ion in liquid phase on both the biomasses was explicitly explained by pseudo second-order model.

Ozdemir et al. (2009) performed the study on the biosorption of zinc. The authors used the linear form of pseudo first and pseudo second-order models to explain the biosorption of zinc ion in liquid phase on the surface of *Geobacillus toebii* and *Geobacillus thermoleovorans*. Results of the investigation evidenced that pseudo second-order model has better suitability to explain the sorption of zinc on the surface of *Geobacillus toebii* and *Geobacillus thermoleovorans*. The values of correlation coefficients for the pseudo second-order model were quite higher compared to pseudo first order model. The research also concluded that the difference between theoretical uptake capacity and experimental uptake capacity in case of pseudo second-order model was quite small, whereas the difference in the theoretical uptake capacity and experimental uptake capacity in case of pseudo first order model was quite higher.

Assuming the binding of metal ions with adsorbate molecule by chemisorption mechanism, the non-linear form of pseudo second-order model has been represented in Eq. (12) (Abdelwaha 2007; Khambhaty et al. 2009)

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = K_2(q_\mathrm{e} - q_\mathrm{t})^2. \tag{12}$$

Integrating Eq. (6) at boundary conditions reproduces Eq. (13)

$$\frac{t}{q_\mathrm{t}} = \frac{t}{q_\mathrm{e}} + \frac{1}{K_2 q_\mathrm{e}^2}. \tag{13}$$

Extrapolation of the plot between t/q_t and t calculates the value of K_2 and q_e as intercept and slope of the curve, respectively.

Mechanistic modeling Convective mass transfer of metal ions in cylindrical coordinates of liquid phase together with mesoporous openings present on biomass is a three-phase mediated process consisting of (1) transport of metal ions from bulk liquid phase including boundary layer to the surface of biomass known as film diffusion, (2) binding of metal ions onto surface of biomass, this step is quite rapid, and (3) transport of metal ions inside the pores of biomass across liquid filled inside pores or by solid phase diffusion from one binding active site to another.

Intra particle model Intra particle model is well documented in various literatures. Mishra et al. (2010, 2011a, b, c) studied the intra particle model very extensively. The authors concluded that alone intra particle model itself was not capable of explaining the biosorption of zinc ion in liquid phase at various stages of adsorption process.

These evidences led to the conclusion that intra particle diffusion is not the only rate-determining step in biosorption of zinc ions. Equation (14) represents linearized form of intra particle diffusion model (Vaghetti et al. 2008)

$$q_\mathrm{e} = K_\mathrm{id}(t)^{0.5} + I \tag{14}$$

where K_id is intra particle diffusion constant and I is the intercept of the model. The value of I in the model indicates the thickness of liquid film around the adsorbent particle.

Bangham's model Very scarce study has been made on the study of Bangham's model. Mishra et al. (2011a, b, c,

2012a, b) studied Bangham's model extensively. The authors concluded that better suitability of the Bangham's model exists to interpret the sorption of zinc ion in liquid phase on the surface of *Cedrus deodara* sawdust against intra particle model. Next approach to elucidate the rate-determining step of zinc ion biosorption onto surface of CDS led to implementation of Bangham's model. Equation (15) (Srinivasan and Hema 2009) represents the linearized form of Bangham's model.

$$\log\left|\log\left\{\frac{C_0}{C_0 - qm}\right\}\right| = \log\left(\frac{K_0 m}{2.303V}\right) + \alpha\log(t) \qquad (15)$$

where q is uptake capacity at time (t), m is mass of biomass in grams, V the volume of solution in liters, $\alpha > 1$ and K_0 are constants. If the data suit well into Eq. 15, then it can be concluded that the film diffusion was the rate-controlling step.

Future recommendation

In future, the biosorption potential of many more adsorbents/biosorbents can be explored to provide a better solution for the removal of metal ions in liquid phase. Process like simultaneous biosorption and bioaccumulation of metal ions is required to be practised more extensively, which ultimately will lead to the increased efficiency of biosorption process. This investigation also recommends that isolation and purification of metal-resistant microbial strains should be explored more efficiently by visiting metal contaminated sites.

Conclusion

After the study of this literature review and keeping a track on the increasing repertoire of publication in biosorption field, it is concluded that the biosorption of heavy metals has been extensively studied on various sorts of biomass. An exhaustive research had been made on the data modeling with the help of isotherm, kinetic and mechanistic models. However, there had been tremendous growth in the field of biosorption, yet very scarce research has been done on the usage of immobilized microbial strain and continuous column study. Moreover, the research in the field of biosorption has many more fruitful possibilities, which yet remain to be investigated and endeavored. Perhaps, the research in the field of bacterium cell immobilization on the surface of biomass is quite scarce. The lacunae in this field have to be reinforced thoroughly to make biosorption a potent clean green technology. In addition to this, a more thorough work is required in terms of column study, so that a more generous solution for treatment of wastewater can be chalked out for industrial partners.

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